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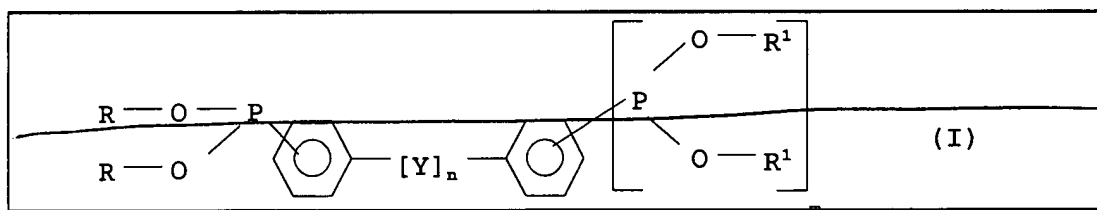
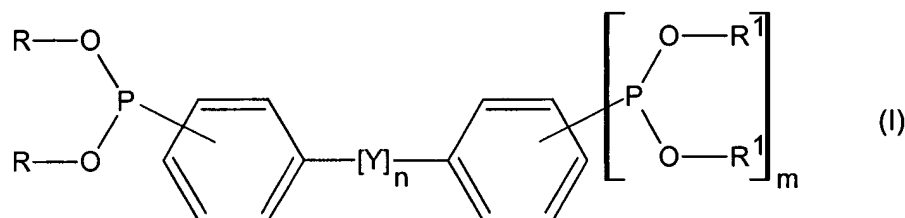
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CLAIMS

1. (currently amended) A thermoplastic molding composition comprising

- A) from 1 to 97.85% by weight of at least one thermoplastic polyester,
- B) from 1 to 97.85% by weight of at least one polycarbonate,
- C) from 1 to 50% by weight of an elastomeric polymer,
- D) from 0.1 to 5% by weight of a phosphorus-containing stabilizer, wherein component D) is composed of an organic phosphonite of the formula (I):



where

m is 0 or 1,

n is 0 or 1,

Y is an oxygen bridge, a sulfur bridge or a 1,4-phenylene bridge, or a bridging unit of the formula $-\text{CH}(\text{R}^2)-$; each of the R-O- and R¹-O-groups, independently of one another, is the radical of an

aliphatic, alicyclic or aromatic alcohol which may contain up to three hydroxyl groups, but excluding any arrangement of the hydroxyl groups which permits these to be part of a phosphorus-containing ring (termed monovalent R–O–groups), or two R–O– or, respectively, R¹–O– groups, bonded to a phosphorus atom, in each case independently of one another, together are the radical of an aliphatic, alicyclic or aromatic alcohol having a total of up to three hydroxyl groups (termed bivalent R–O–, or, respectively, R¹–O–groups),

R² is hydrogen, C₁–C₈–alkyl or a group of the formula COOR³, and

R³ is C_{1–8}–alkyl

or is composed of at least one inorganic salt of phosphoric acids,

E) from 0.05 to 2 % by weight of an organic acid, and

F) from 0 to 60% by weight of other additives ~~other conventional additives~~,

where the percentages by weight of components A) to F) give 100%.

2. (original) A thermoplastic molding composition as claimed in claim 1, wherein

component A) is composed of a polyalkylene terephthalate having from 2 to 10 carbon atoms in the alcohol moiety.

3. (previously presented) A thermoplastic molding composition as claimed in claim 1,

wherein component E) is composed of citric acid or of p-toluenesulfonic acid or

Weber et al., Serial No. 10/018,341

of mixtures of these.

4-5. (canceled)

6. (previously presented) A molding of any type, obtainable from the thermoplastic molding compositions as claimed in claim 1.

Ullmann's Encyclopedia of Industrial Chemistry

Fifth, Completely Revised Edition

Volume A 20:

Photography to Plastics, Processing

Editors: Barbara Elvers, Stephen Hawkins, Gail Schulz



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4.2. Additives [5], [70] (→ Plastics, Additives)

4.2.1. Overview

Polymers are rarely used directly as materials. They do not fulfill per se all technological requirements and become commercially useful only after they have been mixed with certain additives. These additives average ca. 23% of the total weight of plastics (Table 15) but may range for individual plastics from 0% (packaging films for food) to 90% (barium ferrite-filled ethylene-vinyl acetate copolymers for magnetizable sealing strips). Their economic value approximates that of plastics because some additives command prices that are a hundred times those of the plastics themselves.

Polymer additives are to be distinguished from *polymer auxiliaries*; the former are added to polymers after the polymerization process, whereas the latter are used for the manufacture of polymers (e.g., polymerization catalysts, emulsifiers, initiators). The free-radical initiators used for the hardening of unsaturated polyesters

are sometimes considered additives (added to the solution of unsaturated polyester molecules in monomers such as styrene) and sometimes auxiliaries (promoting the thermosetting reaction).

Additives are usually subdivided according to their application into process additives and functional additives. Process additives aid the processing of plastics by either stabilizing the chemical composition of polymers (processing stabilizers) or facilitating the processing itself (processing aids). Functional additives stabilize the chemical composition against attacks by environmental agents (stabilizing additives) or improve certain end-use properties (modifiers). Additives may also be classified according to their primary mode of action (chemical or physical). Some additives act in more than one way: a filler or colorant may also be a nucleating agent for crystallization, a pigment may enhance discoloration, etc.

4.2.2. Chemofunctional Additives

Polymers can be attacked by oxygen and ozone during processing and use. The attack generates radicals that cause chain reactions to produce even more radicals. Ultimately, changed chemical compositions, degradation, or cross-linking result. Oxidation is reduced if the accessibility of the oxidizable groups is limited or if radical formation is prevented. Oxygen diffusion into the polymer is slowed by certain coatings that act as mechanical barriers or by additives that diffuse into surface layers and are preferentially oxidized there.

Antioxidants (→ Antioxidants) prevent radical formation, at least during processing and for the targeted lifetime of the plastic. They are subdivided into deinitiators and chain terminators.

Deinitiators prevent the formation of radicals (therefore: preventive antioxidants) and are always used in combination with chain terminators (therefore also called secondary antioxidants). They are further subdivided into peroxide deactivators, metal deactivators, and UV absorbers. Peroxide deactivators (tertiary amines, tertiary phosphines, sulfides) convert hydroperoxides into harmless compounds before they can form radicals. Metal deactivators are chelating agents that form inactive complexes with catalytically active metal species (mainly from Ziegler-Natta polymerizations).

Chain terminators, such as hindered phenols, amines, and anellated hydrocarbons, react with

already formed radical chain (chain-breakers). A combination of terminators often leads to synergistic effects (e.g., carbon black as filler).

Light-induced degradation is prevented by the reduction of the absorption of light. Less light is absorbed if the surfaces are reflective (e.g., carbon black) or if additives are added (e.g., carbon black) which either convert the infrared radiation or chemical compounds into stable states and then

Heat stabilizers prevent the degradation of plastics at high temperatures. Their main application is poly(vinyl chloride) during processing.

Flame retardants prevent the access to burning plastic by blocking burning gases or by "diluting" the burning process by the burning of the plastic (e.g., phosphorus compounds) or water vapor layer are formed (e.g., treated cellulose) during burning; these radicals are removed from the degradation kinetic chain. Phosphorus compounds are oxidized during the burning process to phosphorus oxides, which either are converted by water or catalyze the elimination of the burning process.

The flammability of plastics is characterized by the limiting LOI value indicates the minimum volume fraction of oxygen in the mixture that just allows for ignition with a LOI > 0.225 are called self-extinguishing with LOI > 0.27, self-extinguishing values (high flammability) oxymethylenes (0.14), saturated polyesters (0.18), High LOI values are exhibited by (e.g., tetrafluoroethylene (0.95) not absolute measure: combustibility of plastics also depend on flammability

Table 15. Annual U.S. consumption of polymer additives for plastics, 1980 (plastics production: 16076000 t/a)

Additive	Consumption in t/a
<i>Process additives</i>	
Processing stabilizers	
Heat stabilizers (PVC)	43 000
Antioxidants	18 000
Processing aids	
Lubricants, slip agents, etc.	50 000
Polymeric processing aids	< 1 000
Mold-release agents	< 1 000
Nucleating agents	< 1 000
<i>Radical initiators for thermosets</i>	15 000
<i>Functional additives</i>	
Stabilizing additives	
Antioxidants	see above
Metal deactivators	< 1 000
Light stabilizers	2 400
Flame retardants	220 000
Biostabilizers	< 1 000
Modifiers	
Colorants	150 000
Fillers and reinforcing agents	
Mineral-based	1730 000
Glass	462 000
Natural organic	133 000
Synthetic organic	2 000
Plasticizers	1 000 000
Blowing agents (without gases)	7 000
Impact modifiers	< 5 000
Antistatic agents	2 000
<i>Total</i>	3 844 400

dered additives (added to the polyester molecules in styrene) and sometimes auxiliary thermosetting reaction). Usually subdivided according to process additives and stabilizers. Process additives aid the processing of polymers (processing aids) by either stabilizing the polymer or by facilitating the processing itself. Functional additives stabilize the polymer against attacks by environmental agents (stabilizing additives) or improve properties (modifiers). Additives are classified according to their function (chemical or physical). In more than one way: a filler can be a nucleating agent for polymers; a pigment may enhance discoloration.

Functional Additives

be attacked by oxygen and processing and use. The attack that cause chain reactions to radicals. Ultimately, degradation, or cross-linking is reduced if the accessible groups is limited or if prevented. Oxygen diffusion is slowed by certain coatings or barriers or by additives on surface layers and are preferred.

Antioxidants prevent radical attack during processing and for life of the plastic. They are stabilizers and chain terminators. Prevent the formation of radical (preventive antioxidants) and are in combination with chain terminators called secondary antioxidants. Further subdivided into peroxide, metal deactivators, and peroxide deactivators (tertiary phosphines, sulfides) convert to harmless compounds before radicals. Metal deactivators are that form inactive complexes with active metal species (mainly in polymerizations). Others, such as hindered phenols, substituted hydrocarbons, react with

already formed radicals and terminate the kinetic chain (chain-breaking or primary antioxidants). A combination of deinitiators and chain terminators often leads to synergistic effects. Antagonistic effects are also known (e.g., with carbon black as filler).

Light-induced degradation reactions can be prevented by the reduction of light absorption or by the addition of *UV absorbers* and quenchers. Less light is absorbed by the plastic if the surfaces are reflective or if certain pigments are added (e.g., carbon black). Ultraviolet absorbers either convert the incident light into harmless infrared radiation or are transformed into other chemical compounds. Quenchers deactivate excited states and themselves become excited.

Heat stabilizers prevent chemical transformations of plastics at higher temperature; their main application is for the stabilization of poly(vinyl chloride) against HCl elimination during processing.

Flame retardants either prevent oxygen access to burning plastics by formation of non-burning gases or by "poisoning" radicals generated by the burning. Some plastics are self-extinguishing because either CO₂ (polycarbonates) or water vapor and a protecting carbon layer are formed (vulcanized fiber: a ZnCl₂-treated cellulose) during burning. Chlorine and bromine compounds generate radicals during burning; these radicals combine with radicals from the degradation of plastics and stop the kinetic chain. Phosphorus compounds are oxidized during the burning to nonvolatile phosphorus oxides, which either form a protective layer or are converted by water into phosphorus acids that catalyze the elimination of water.

The flammability of plastics is often characterized by the limiting oxygen index (LOI). The LOI value indicates the limiting value of the volume fraction of oxygen in an oxygen-nitrogen mixture that just allows the polymer to burn after ignition with a flame. Materials with LOI > 0.225 are called flame retardant; those with LOI > 0.27, self-extinguishing. Low LOI values (high flammabilities) are exhibited by polyoxymethylenes (0.14), polyolefins (0.17–0.18), saturated polyesters (0.20), and cellulose (0.20). High LOI values are exhibited by poly(vinyl chloride) (0.32), polybenzimidazole (0.48), and polytetrafluoroethylene (0.95). However, LOI values are not absolute measures of the flammability or combustibility of plastics because these properties also depend on flame temperatures, heat ca-

pacities, heat conductivities, melting temperatures, and melt viscosities. The hazard of burning plastics is also determined by smoke formation and the toxicity of the evolving gases.

4.2.3. Processing Aids

Processing aids facilitate the processing of plastics by enhancing either transport rates to the processing machines, flow behavior in these machines, achievement of final properties during processing, or removal of shaped articles from the machines or from each other.

Easy-flow grades of powdered polystyrenes, for example, often contain 3–4% mineral oil, which forms a low-viscosity film on the surface of the particles and thus reduces friction in polymer machines; amphiphilic compounds such as metal stearates or fatty acid amides are used for this purpose. Such *external lubricants* also reduce the friction between polymer particles and the walls of the processing machine and the friction of polymer melts at such walls; they also prevent the cleavage of particles to smaller flow units. External lubricants are always incompatible with polymers and are thus found predominantly at polymer surfaces. They are related to *release agents*, which facilitate the separation of shaped articles from the tools (molds), and *slip agents*, which prevent the sticking together of shaped articles. Slip agents are thus sometimes also called lubricants.

Internal lubricants improve the flow behavior and homogeneity of polymer melts; they also reduce the Barus effect (see Section 7.3.2) and the melt fracture. Internal lubricants probably act by desegregating larger units (aggregates), which were probably formed during polymerization and are still present shortly after the melting of the polymer to a macroscopically homogeneous material. Typical internal lubricants are amphipolar compounds, e.g., modified esters of long-chain fatty acids.

Nucleating agents promote the crystallization of crystallizable polymers by generating many nuclei for crystallites. They prevent the formation of larger spherulites and thus improve the mechanical properties of plastics.

4.2.4. Extending and Reinforcing Fillers

Fillers are solid inorganic or organic materials. Some fillers are added mainly to improve the

economics of expensive polymers; they are *extenders*. Extenders are usually particulate materials of corpuscular nature, such as chalk and glass spheres (aspect ratio ca. 1). Other fillers are *reinforcing agents* ("active fillers"); they improve certain mechanical properties. Reinforcing agents possess aspect ratios higher than 1; they may be short fibers, platelets (e.g., kaolin, talc, mica) (\rightarrow Reinforced Plastics), or long fibers (continuous filaments). Active fillers are sometimes subdivided into property enhancers (aspect ratio < 100) and true reinforcing fillers (aspect ratio > 100). No sharp dividing line exists between fillers and reinforcing agents, nor can the term "reinforcement" be unambiguously defined (e.g., it may denote an increase in breaking or impact strength or a decrease of brittleness).

A variety of fillers are used for plastics (Table 16).

Glass-fiber-reinforced polymers often carry the abbreviation GRP (or FRP); those reinforced

by synthetic organic fibers, CRP. Syntactic plastics are polymers reinforced with hollow glass spheres. The amounts of fillers added vary widely: in general, industry standards are about 30 wt% for thermoplastics and 60 wt% for thermosets.

Fillers act very differently in polymers. Some fillers form chemical bonds with polymers; an example is carbon black, which acts as a chemical cross-linker in elastomers. Other fillers can adsorb polymers on their surfaces: that is, physical bonds are introduced between fillers and polymers. On impact, adsorbed chain segments may take up energy and slip from the surface, which increases impact strength. Still other fillers act as nucleating agents in crystallizable polymers. Fillers furthermore constitute impenetrable walls to polymer coils. They restrict the number of conformational positions of chain segments near the filler surface; chains become less flexible, and tensile strengths and moduli of elasticity increase.

4.2.5. Plasticizers (\rightarrow Pl

Plasticizers are added to their flexibility, processing. About 500 different types are known. They are generally liquids; polymer plasticizers are in smaller amounts. Of all thermoplastics, 80–85% are plasticized (e.g., with phthalic chloride); the most important is (2-ethylhexyl)phthalate (DOP). The main plasticizer for mineral oil; tires contain plasticizers are mainly aliphatic polyethers. The former are used in high temperatures; they thus possess mass distributions and average molar mass is low. They are called oligomer plasticizers. This can also be achieved by copolymerization of the parent monomer with comonomers; this effect is called internal plasticization and low molar mass plasticizers.

External plasticizers are primary and secondary ones. Primary ones interact directly with chains. Secondary plasticizers are used only in combination with primary plasticizer. A certain plasticizer is a primary or a secondary plasticizer depending on its chemical constitution of oils are, for example, polydienes but extender (e.g., stearic acid).

4.2.6. Colorants

Colorants are subdivided into pigments (in polymer matrix) and dyes (in solution). Pigment fibers are dyed mainly for plastics because of their lightfastness and are more expensive than dyes. Colorants are often named by titanium dioxide (TiO₂) black (20%); only 2% are organic pigments.

Pigment particles generally have diameters of 0.3–0.8 μm , which allows them to be used in films and fibers of $> 20\text{-}\mu\text{m}$ thickness. Films and fibers are colored by pigments because these have smaller diameters than in

Table 16. Fillers for thermoplastics (T), thermosets (D), and elastomers (E). For definition of other acronyms see Table 1

Filler	Application in	Concentration in %	Improved property
<i>Inorganic fillers</i>			
Chalk	PE, PVC, PPS, PB, UP	< 33 in PVC	price, gloss
Potassium titanate	PA	40	dimensional stability
Heavy spar	PVC, PUR	< 25	density
Talc	PUR, UP, PVC, EP, PE, PS, PP		white pigment, impact strength, plasticizer uptake
Mica	PUR, UP	< 25	dimensional stability, stiffness, hardness
Kaolin	UP, vinyls	< 60	demolding
Glass spheres	T, D	< 40	modulus of elasticity, shrinkage, compressive strength, surface properties
Glass fibers	T, D	< 40	fracture strength, impact strength
Fumed silica	T, D	< 3	tear strength, viscosity (increase)
Quartz	PE, PMMA, EP	< 45	heat stability, fracture
Sand	EP, UP, PF	< 60	shrinkage (decrease)
Al, Zn, Cu, Ni, etc.	PA, POM, PP	< 100	conductivity (heat and electricity)
MgO	UP	< 70	stiffness, hardness
ZnO	PP, PUR, UP, EP	< 70	UV stability, heat conductivity
<i>Organic fillers</i>			
Carbon black	PVC, HDPE, PUR, PI, PE, E	< 60	UV stability, pigmentation, cross-linking
Graphite	EP, MF, PB, PI, PPS, UP, PMMA, PTFE	< 50	stiffness, creep
Wood flour	PE, MF, UF, UP	< 5	shrinkage (decrease), impact strength
Starch	PVAL, PE	< 7	biological degradation

fibers, CRP. Syntactic plastic reinforced with hollow glass; of fillers added vary widely; standards are about 30 wt% and 60 wt% for thermosets. Differently in polymers. Some bonds with polymers; an tack, which acts as a chemilastomers. Other fillers can their surfaces: that is, produced between fillers and t, adsorbed chain segments and slip from the surface, tect strength. Still other fillers gents in crystallizable polymore constitute impenetracoils. They restrict the numional positions of chain iller surface; chains become sile strengths and moduli of

4.2.5. Plasticizers (→ Plasticizers)

Plasticizers are added to polymers to improve their flexibility, processability, or foamability. About 500 different types of plasticizers are marketed. They are generally low molar mass liquids; polymer plasticizers are used in much smaller amounts. Of all plasticizers for thermoplastics, 80–85% are used for poly(vinyl chloride); the most important plasticizer is di-(2-ethylhexyl)phthalate ("dioctyl phthalate," DOP). The main plasticizer for elastomers is mineral oil; tires contain up to 40%. Polymer plasticizers are mainly aliphatic polyesters and polyethers. The former are prepared by polycondensation; they thus possess fairly broad molar mass distributions and also contain monomeric and oligomeric molecules. Since their number-average molar mass is low (ca. 4000 g/mol), they are called oligomer plasticizers. Plasticization can also be achieved by copolymerization of the parent monomer with certain other monomers; this effect is called internal plasticization, in analogy to external plasticization by added high and low molar mass plasticizers.

External plasticizers are subdivided into primary and secondary ones. Primary plasticizers interact directly with chains by way of solvation. Secondary plasticizers are merely extenders; they can be used only in combination with a primary plasticizer. A certain plasticizer may thus be a primary or a secondary one, depending on the chemical constitution of the polymer. Mineral oils are, for example, primary plasticizers for polydienes but extenders for poly(vinyl chloride).

4.2.6. Colorants

Colorants are subdivided into dyes (soluble in polymer matrix) and pigments (insoluble). Textile fibers are dyed mainly with dyes. Pigments are preferred for plastics because they have a higher lightfastness and are more stable against migration than dyes. Colorants for plastics are dominated by titanium dioxide (60–65%) and carbon black (20%); only 2% are dyes.

Pigment particles generally possess diameters of 0.3–0.8 μm , which allows the pigmentation of films and fibers of > 20- μm thickness. Very thin films and fibers are colored exclusively by organic pigments because these can be ground to much smaller diameters than inorganic ones. The hid-

ing power of pigments increases with increasing difference between refractive indices of pigment and polymer.

Pigments need not have a special affinity for polymers. They must be wettable by the polymer melt, however, which can be achieved by treating them with surfactants. The aggregation of pigments is mainly the result of air inclusions; it can be removed by the application of vacuum. Pigments can be metered into plastics via master batches (in plastics), color concentrates (in plasticizers), or electric charging of the surface of polymer particles in granulate mixers. Up to 1 wt% of pigment can be mixed in by the last method.

4.2.7. Blowing Agents

Foamed plastics (plastic foams, cellular plastics, expanded plastics) are blends of polymers with gases (→ Foamed Plastics). They may be rigid (glass transition or melting temperature higher than use temperature) or flexible; their cell structure can be open or closed. The gases may be air, nitrogen, carbon dioxide, fluorinated hydrocarbons, etc.

Plastic foams can be produced by mechanical means (whipping, stirring), physical methods (shock volatilization of liquids, washing-out of solids), or chemical foaming either by internal foaming during the polymerization or by external foaming with chemical blowing agents. Chemical blowing agents are chemical compounds that decompose at elevated temperature with release of gases. The most widely used agent for natural rubber is *N,N'*-azobisisobutyronitrile $(\text{CH}_3)_2\text{C}(\text{CN})-\text{N}=\text{N}-\text{C}(\text{CN})(\text{CH}_3)_2$ (AIBN); for plasticized PVC, *N,N'*-dinitroso dimethyl terephthalamide $\text{CH}_3-\text{N}(\text{NO})-\text{CO}-(p-\text{C}_6\text{H}_4)-\text{CO}-\text{N}(\text{NO})-\text{CH}_3$ (NTA); and for other plastics, 1,1'-azobisformamide $\text{H}_2\text{N}-\text{CO}-\text{N}=\text{N}-\text{CO}-\text{NH}_2$ (ABFA). Blowing agents are used in amounts of ca. 0.1% to eliminate sinks in injection molding; 0.2–0.8% for injection-molded structural foams; 0.3% for extended profiles; 1–15% for vinyl plastisol foaming; and 5–15% for compression-molded foam products.

4.3. Processing

Many different types of processes exist to convert monomers, prepolymers, or polymers

ion of other acronyms see Table 1

%	Improved property
	price, gloss
	dimensional stability
	density
	white pigment, impact
	strength, plasticizer uptake
	dimensional stability, stiffness, hardness
	demolding
	modulus of elasticity, shrinkage, compressive strength, surface properties
	fracture strength, impact strength
	tear strength, viscosity (increase)
	heat stability, fracture shrinkage (decrease)
	conductivity (heat and electricity)
	stiffness, hardness
	UV stability, heat conductivity
	UV stability, pigmentation, cross-linking
	stiffness, creep
	shrinkage (decrease), impact strength
	biological degradation

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The glass transition temperature of BPA-PC can be increased even further by partial or total replacement of bisphenol A by 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane [8]; glass transition temperatures of ca. 150 to 240°C can be achieved in this way. These polycarbonates are transparent, tough, and colorless, even at high glass transition temperatures [8]. Their melt viscosities are favorable compared with those of aromatic polyester carbonates, polysulfones, polyethersulfones, and polyetherimides having the same glass transition temperature.

BPA-PC is used in polymer blends (→ Polymer Blends, pp. 292–294). The most important blends are those with acrylonitrile–butadiene–styrene (ABS) graft polymers [6], [19], [20] and those with poly(butylene terephthalate) or poly(ethylene terephthalate), and impact resistance modifiers (e.g., ABS) [6], [19], [21]. Compared to ABS, BPA-PC–ABS blends have improved heat resistance. They also exhibit good processibility, light stability, surface quality, and high toughness, even at low temperature (tough fracture in the notched impact strength test). Blends of BPA-PC with poly(alkylene terephthalates) and impact strength modifiers have a high heat distortion resistance, and high toughness even at low temperature. Their resistance to gasoline and other solvents is better than that of BPA-PC.

2.3. Bisphenol A Polycarbonate with Additives

Most of the additives discussed in this section are described in detail elsewhere (→ Plastics, Additives).

Mold-Release Agents. The addition of small amounts (< 1 wt %) of mold-release agents (e.g., fatty acid esters of higher alcohols, such as pentaerythritol or glycerol) to the polycarbonate improves the mold release of complicated parts [6]. See also → Release Agents.

Flame Retardants. The flame resistance of BPA-PC can be increased by incorporating tetrabromobisphenol (see Section 2.2) or by using additives or additive combinations [6]. For example, flame resistance is significantly improved by the addition of small amounts (< 1 wt %) of special salts, such as potassium perfluoro-*n*-butane-1-sulfonate, sodium 2,4,5-trichloroben-

zenesulfonate, and potassium diphenylsulfone-3-sulfonate [22]–[25]. The tendency to form flaming drips after ignition can be reduced by using branched polycarbonates (see Section 2.2) or by adding small amounts (< 1 wt %) of polytetrafluoroethylene [26].

Light Stabilizers. Ultraviolet light, especially in combination with atmospheric oxygen and moisture, causes decomposition of BPA-PC. Decomposition starts with a photo-Fries rearrangement, which leads to the formation of salicylates, followed by benzophenones [6], [7]. These structures absorb visible light in the short-wavelength region and are thus responsible for the yellowing of polycarbonates. Stabilization against degradation by UV light (i.e., against yellowing) is important for exterior uses and applications and can be achieved by adding small amounts (< 1 wt %) of benzotriazole derivatives [7].

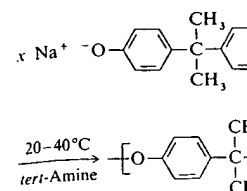
Reinforcement. Glass fibers (< ca. 35 wt %) are generally added to the polycarbonate for reinforcement. They improve rigidity and stiffness, and lower the coefficient of thermal expansion [6], [7], [27].

Miscellaneous Additives. *Heat stabilizers* (e.g., organic phosphites) can be added to the polycarbonate to prevent thermal oxidation during processing at high temperature [6]. *Blowing agents* (e.g., 5-phenyltetrazole and phenyldihydro-oxadiazonone) can be added during thermoplastic processing into moldings to obtain low-weight foamed structures (→ Foamed Plastics, A 11, p. 458) [6]. Transparent or opaque polycarbonates can be obtained in a wide range of colors by using *organic dyes* and *inorganic pigments*.

3. Production

3.1. Interfacial Polycondensation

Interfacial polycondensation is currently used for the industrial production of polycarbonates [2], [5], [6]. Bisphenol A is reacted with phosgene at 20–40°C in a two-phase mixture consisting of an aqueous, alkaline phase and an immiscible organic phase. The overall reaction is as follows:



The bisphenol A in aqueous phase as sodium phosgene is dissolved in generally consists of chloroform (e.g., dichloromethane) phase interface to produce which then enter the 20 mol % excess of phosgene amount of bisphenol A, a small proportion of hydrolyzed. The hydrolyzed Na_2CO_3 enter the aqueous phase at low pH values (9–11) a generation to minimize p

After the formation a catalyst is added. Triethylamine (e.g., triethylamine, triethylamine) are preferred to catalyze the polycondensation of high molecular mass polycarbonates. Hydrolysis of excess phosgene groups formed due to this is important because phosgene contained in these corrode the molds used for processing. During the processing the aqueous phase values (9–14).

Monofunctional phenol or 4-*tert*-butylphenol A) are added as two-phase mixture before catalyst, to control the molecular weight of the polycarbonate then form the polycarbonate bound.

Polycarbonate production batchwise in stirred tank reactors which the organic and distributed by shear force polycondensation, the organic phase which contains sodium carbonate, is separated from the aqueous phase by centrifugation. The organic phase is washed with dilute acid

The water content [2.76] is also of great importance for the processing of thermoplastic polyesters because water often causes hydrolytic decomposition at high processing temperatures (see p. 241). The equilibrium water content, for a given degree of polymerization \bar{P}_n must not be exceeded on account of the danger of hydrolytic decomposition. This content can be calculated for high conversions from the approximate formula

$$\bar{P}_n = \sqrt{\frac{K}{n_{H_2O}}}$$

\bar{P} where K is the equilibrium constant and n_{H_2O} denotes the number of moles of water per mole of monomer. For example, the maximum water content for PETP ($K \approx 4$) with a molecular mass $M_n \approx 10000$ ($\bar{P}_n = 100$) is 0.01 wt %.

A further criterion for the use of thermoplastic polyesters in the fiber or plastics sector is the intrinsic color. This is usually specified as a blue-yellow value (measured with an electric remission photometer) [2.77].

2.4. Co-Components and Additives [2.78]

Thermoplastic Copolyesters. The dyeability, elasticity, pilling behavior, shrinkage, hydrophilicity, and flame resistance of polyester fibers can be improved by condensation with appropriate comonomers [2.79].

The crystallinity, melting point, glass transition temperature, elasticity, flammability, solubility, and other properties of thermoplastic polyesters used in the plastics sector can be modified by selective co-condensation.

Examples of such copolyesters are glass-clear (amorphous) copolyesters based on 1,4-cyclohexanedimethanol, terephthalic acid, and isophthalic acid (i.e., poly(1,4-cyclohexylenedimethylene terephthalate-co-isophthalate) [26124-27-6] [2.80]); elastic copolyesters based on 1,4-butanediol, poly(tetrahydrofurandiol), and terephthalic acid (i.e., poly(butylene terephthalate-co[multibutyleneoxy] terephthalate) [2.53], [2.54]; neopentyl-glycol-containing copolyesters with good solution properties in paint solvents [2.81]; and copolyesters based on 1,4-butanediol, terephthalic acid, and isophthalic acid with relatively low melting points for hotmelt adhesives [2.82]. Thermoplastic copolyesters with elevated glass transition temperatures (and thus im-

proved heat resistance) can be obtained by incorporating heterocyclic diols during condensation [2.83]. For the production of copolyesters, see p. 238.

Additives. Raw polymers are seldom processed as such into semifinished or finished articles. Additives are usually added to the polymers in a process known as compounding or formulation. Compounding processes (e.g., mixing, kneading, extrusion, pelletization) are of great importance because the properties, processing, and use of thermoplastic polymers are substantially determined by the additives (e.g., nucleating agents, fillers, flame retardants, stabilizers, pigments).

Nucleating Agents [2.84], [2.85]. See also → Plastics, Additives, A 20, pp. 500–501. The processibility of PETP in injection molding is mainly determined by its slow crystallization rate and by the associated danger of cold crystallization (tendency to distortion). High molding temperatures (ca. 140°C) and addition of nucleating agents are therefore necessary to accelerate the nucleation rate. Inorganic substances such as talc, magnesium oxide, or clay are added as nucleating agents in concentrations of 0.001–1% with a maximum particle size of 2–3 μm. Organic compounds include salts of aromatic carboxylic acids, fatty acid salts, Montan waxes, and polymers such as polyethylene. The nucleating agents can be added at any stage during PETP production or as a powder to the granulate.

PBT and PBT copolyesters with polytetrahydrofuran generally crystallize so rapidly that nucleation is not necessary.

Glass Fibers [2.86]. See also → Plastics, Additives, A 20, pp. 494–497. The heat resistance, rigidity, and hardness of thermoplastic polyesters can be considerably increased by adding glass fibers or beads. For example, the heat distortion temperature (according to Martens, DIN 53458) of PBT reinforced with glass fiber varies as follows:

Heat distortion temperature, °C	50	75	120	160	190
Glass fiber content, wt %	0	10	20	30	50

The glass reinforcement may be added as beads, ground glass fiber, staple glass fiber, or long glass fiber. Maximum heat resistance, rigidity, and hardness are achieved by adding long glass fibers. These additives are mixed with the thermoplastic polyesters in special extruders in a separate compounding stage; amounts of up to 50% are commonly employed.

Flame Retardants. See also → Flame Retardants, and → Plastics, Additives, A 20, pp. 483–494. Thermoplastic polyesters (PETP and PBT) have a relatively low flammability because they escape the action of the flame due to melting and droplet formation (oxygen index of PBT, 23%; UL 94 rating, HB); see also → Flame Retardants, A 11, p. 127). Fillers and, in particular, glass fiber reinforcement prevent droplet formation, resulting in a sharp increase in flammability (oxygen index of PBT reinforced with 10% glass fiber, 19%). Legislation is increasingly promoting the use of self-extinguishing, nondrip plastics formulations.

Self-extinguishing thermoplastic polyesters are obtained by incorporating ca. 30% of flame retardants, which are usually aromatic halogenated compounds combined

with antimony [2.88] (see also p. 238). Examples are brominated polyethylenes [2.90], or ethylene with antimony and antimony [2.91].

The flame retardancy of the production sequence compounds.

The polybrominated compounds producing polyfurans in the esterification are no longer used in the plastics sector. The use of retardants has given rise to developments in the plastics sector, such as microencapsulated polyphosphates, carbonate have been used in the plastics sector, but are not added in the plastics sector.

Flame retardants are added in the plastics sector.

Stabilizers. See also → Plastics, Additives, A 20, pp. 461–475. In polyetheresters, the decomposition products include sterically hindered compounds added to the plastics sector, 0.5 wt % or are added to the plastics sector.

The antioxidants have been used in the plastics sector, but are not added in the plastics sector.

Pigments [2.87]. See also → Plastics, Additives, A 20, pp. 494–497. The heat resistance, rigidity, and hardness of thermoplastic polyesters can be considerably increased by adding glass fibers or beads. For example, the heat distortion temperature (according to Martens, DIN 53458) of PBT reinforced with glass fiber varies as follows:

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stance) can be obtained by incorporating cyclic diols during condensation production of copolyesters, see

low polymers are seldom processed unfinished or finished articles. Additionally added to the polymers in a compounding or formulation processes (e.g., mixing, kneading, extrusion) are of great importance. Properties, processing, and use of polymers are substantially determined by additives (e.g., nucleating agents, flame retardants, stabilizers, pigments).

Flame Retardants [2.84], [2.85]. See also → Plastics, pp. 500–501. The processibility of PETP is mainly determined by its slow crystallization (due to the associated danger of cold crystallization to distortion). High molding temperature and addition of nucleating agents are used to accelerate the nucleation rate. Inorganic as talc, magnesium oxide, or clay are used as agents in concentrations of 0.001–1% (particle size of 2–3 μm). Organic compounds of aromatic carboxylic acids, fatty acids, waxes, and polymers such as polyethylene glycol can be added at any stage of processing or as a powder to the granulate. Copolyesters with polytetrahydrofuran crystallize so rapidly that nucleation is not neces-

sary [2.86]. See also → Plastics, Additives, pp. 483–494. The heat resistance, rigidity, and hardness of polyesters can be considerably improved by glass fibers or beads. For example, the glass transition temperature (according to Martens, DIN 53480) with glass fiber varies as follows:

Temperature, °C	50	75	120	160	190
Glass fiber, wt%	0	10	20	30	50

Forcement may be added as beads, staple glass fiber, or long glass fiber. The heat resistance, rigidity, and hardness are improved by long glass fibers. These additives are used in copolyesters in special extrusion compounding stage; amounts of up to 50% are employed.

Flame Retardants. See also → Flame Retardants, pp. 483–494. Thermoplastic polyesters (PETP and PBT) have a relatively low glass transition temperature because they escape the action of the flame by droplet formation (oxygen index of PETP, 17; PBT, 19); see also → Flame Retardants. Fillers and, in particular, glass fiber prevent droplet formation, resulting in a high flame resistance (oxygen index of PBT reinforced fiber, 19%). Legislation is increasing the use of self-extinguishing, nondrip plas-

tics. Thermoplastic polyesters are obtaining ca. 30% of flame retardants, which are halogenated compounds combined

with antimony oxide [2.87] or with phosphorus compounds [2.88] (see also → Flame Retardants, A 11, p. 123). Examples are brominated polycarbonates [2.89] and polystyrenes [2.90], or ethylene(tetrabromophthalimide) in combination with antimony oxide. A combination of red phosphorus and antimony oxide is also used, particularly with PETP [2.91].

The flame retardants are not normally added during the production of thermoplastic polyesters, but in a subsequent compounding stage.

The polybrominated diphenyl ethers are suspected of producing polybrominated dibenzodioxins and dibenzofurans in the event of fire [2.92]; they are therefore no longer used in Germany, and interest in halogen-free flame retardants has greatly increased. Up to now, however, only developments and improvements of conventional systems, such as microencapsulated red phosphorus, ammonium polyphosphates, magnesium hydroxide, and magnesium carbonate have been described [2.93], [2.94]. The magnesium compounds have the disadvantage that they have to be added in substantially higher amounts and may therefore seriously affect the polymer properties.

Fully aromatic liquid crystalline polyesters have a low flammability and do not require flame retardants.

Stabilizers. See also → Plastics, Additives, A 20, pp. 461–475. In contrast to PETP and PBT, thermoplastic polyetheresters are extremely sensitive to photooxidative decomposition [2.95] and must be stabilized. Stabilizers include sterically hindered phenols or amines, which are added to the starting substances in an amount of 0.1–0.5 wt% or are incorporated in the polymer melt [2.96].

The antioxidant 4,4'-bis(α,α'-dimethylbenzyl)diphenylamine has been approved by the FDA for use in phthalate, isophthalate, and terephthalate polyesters with 1,4-butanediol and polytetrahydrofuran.

Pigments [2.97], [2.98]. Pigments with an adequate heat resistance (e.g., titanium dioxide, carbon black, phthalocyanines, quinacridones, cadmium yellow) are suitable for coloring thermoplastic polyesters.

Admixture of Other Polymers. The properties of partially aromatic thermoplastic polyesters can be selectively improved by blending with other polymers. See also, → Polymer Blends, p. 294. PBTs whose impact properties have been improved with polybutadiene graft rubbers are used in car bumper systems [2.99]. Impact strength can also be increased by adding polyethylene [2.100]. Higher flexibility is obtained by blending with polyether elastomers [2.101].

New alloying components such as styrene-maleic anhydride copolymers or acrylonitrile-styrene-acrylate copolymers also expand the application range, particularly of PBT [2.102]. Polymer blends of bisphenol-A-polycarbonate with PBT or PETP have good low-temperature strength and low shrinkage values, they have been commercially successful for several years [2.103].

Blends with polyurethanes and polyamides [2.104] or poly-ε-caprolactone [2.105] are also described.

2.5. Properties

The properties of thermoplastic polyesters depend primarily on the starting compounds (dicarboxylic acids, diols), their molecular mass, and added fillers. The properties of PETP, PBT, and PDCT as fiber raw materials are described in → Fibers, 4. Synthetic Organic, A 10, pp. 587, 601, 603.

PETP and PBT. The two most important thermoplastic polyesters for the plastics sector, namely PETP and PBT, can be described as partially crystalline polymers. They have a high hardness and rigidity, good creep strength, high dimensional stability, and very good slip and wear behavior [2.106], [2.107]. Whereas PBT occurs almost exclusively in the partially crystalline form, PETP can also be processed into amorphous molded bodies with high transparency; on heating to 70–100°C this transparency is lost due to postcrystallization. Transparency can, however, be retained if the polyester chains are forcibly oriented, for example by biaxial stretching and heat setting (transparent films of PETP, → Films, A 11, p. 105).

A special property of PETP is its slow crystallization, which necessitates molding temperatures of ca. 140°C and the use of a nucleating agent and crystallization accelerator (see p. 240).

PBT and PETP are resistant to water, weak acids and bases, alcohols, ketones, ethers, aliphatic hydrocarbons, and chlorinated aliphatic hydrocarbons at room temperature.

Solvents for PBT and PETP include hexafluoro-2-propanol, hexafluoroacetone, and 2-chlorophenol (mixed solvents, see Table 2).

Hydrolysis proceeds rapidly in the melt in the presence of moisture. The dependence of the hydrolysis rate on temperature and moisture content has been investigated [2.108], [2.109].

The most important mechanical, thermal, and electrical properties of PETP and PBT are summarized in Table 3.

Polyetheresters [2.110]–[2.112]. Thermoplastic polyetheresters are block copolymers synthesized from mutually incompatible rigid crys-